Separation and Purification Technology 124 (2014) 89–98

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Cleaner recovery of tetrafluoroethylene by coupling residue-recycled polyimide membrane unit to distillation

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ARTICLE INFO

Article history:
Received 16 November 2013
Received in revised form 8 January 2014
Accepted 9 January 2014
Available online 27 January 2014

Keywords:
Tetrafluoroethylene
Polyimide membrane
Gas separation
Selectivity
Optimization

ABSTRACT

Low-boiling-point impurities (CO, N_2 and O_2) strip away a considerable quantity of expensive tetrafluoroethylene (TFE) in the synthesis. The traditional acetone absorption cannot recover TFE satisfactorily, due to the inherent problems of cryogenic operation, complex process, acetone loss and pollution, etc. With the objective of cleanly and economically recovering TFE, the technique of coupling membrane unit to distillation is studied in this work. Polyimide membrane is selected after analyzing gas molecular properties (V_C and T_C). According to the actual permeation test with TFE distillation vent gas at 30 °C, $\alpha_{O2/TFE}$ = 190.6, $\alpha_{N2/TFE}$ = 29.1, $\alpha_{CO/TFE}$ = 23.0, and J_{TFE} = 0.1 GPU. TFE is concentrated in the high pressure residue, after slightly compressing which can be facilely recycled into distillation. Afterwards, process simulation and optimization preparing for the pilot test is fulfilled. For typical 5-kt/a TFE plants with a ± 10% fluctuation, the optimum membrane area falls in the range of 440–550 m^2. The coupled distillation is operated with the original reboil ratio rather than the reflux ratio to refine TFE without consuming much more energy. The coupled membrane system decreases TFE loss to 38 t/a, superior to acetone absorption (50 t/a). Moreover, it can perfectly avoid the negative effect of volatile acetone. Thus, coupling polyimide membrane unit to distillation is a promising technique to improve TFE recovery in the synthesis.

1. Introduction

Tetrafluoroethylene (TFE) is an expensive monomer widely used in manufacturing fluorinated polymers with special properties [1,2]. The main TFE synthesis process is chlorodifluoromethane (R22) pyrolysis at 750–980 °C, with steam as the diluting agent [3–5]. However, the steam causes a disadvantageous reaction that a small amount of fluorocarbon radicals would be hydrolyzed into carbon monoxide (CO) [4]. After steam and acidic gases are removed, the cracking stream usually contains about 1.4–3.5% of CO by volume [5]. Besides, some other low-boiling-point impurities, O_2 and N_2, are introduced into the cracking stream by the feedstock. These impurities are vented at the separation sequence end which is often operated at moderate pressure and low temperature, e.g., 1.30 MPa and −30 °C [6]. Generally, the vent gas contains about 60.0 mol% of TFE. In 5-kt/a TFE synthesis plants, the quantity of TFE stripped away is approximately 450 t per year, resulting in a great economic loss of 5.0 million USD per year roughly.

Traditionally, TFE in the vent gas is recovered by cryogenic acetone absorption [7]. TFE is one order of magnitude more soluble than the light impurities in acetone at −30 °C and 1.30 MPa. TFE can be considerably concentrated by such recovery process; however, the acetone absorption has the following limitations:

a. A large amount of acetone needs to be recycled in the process due to its insufficiently high TFE solubility under the operation conditions, rendering a great demand of refrigeration power.
b. A combined system of absorption tower, desorption tower, heat exchangers, circulating pumps, and compressor is required for the recovery, raising the system complexity and capital cost.
c. The effluent after absorption still contains considerable TFE with content up to 12.0 mol%.
d. Acetone, being volatile, can be stripped away by the low-boiling-point impurities and lost.
e. Acetone can be taken into distillation system by the desorbed gas and affecting TFE quality.

To avoid these problems, membrane separation may be an alternative technique to recover TFE. Gas membrane separation is an important technique rapidly developing in the last three decades. Not involving mobile separating agent and heat transferring for phase transition [8–10], membrane technique can be used to

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http://dx.doi.org/10.1016/j.seppur.2014.01.014

Nomenclature

TFE	tetrafluoroethylene
USD	the United States dollar
V_C	critical volume of gas molecules
T_C	critical temperature of gas molecules
PDMS	polydimethylsiloxane
TFE-BDD87	poly(2,2-trifluoromethyl-4,5-difluoro-1,3-dioxole-*co*-tetrafluoroethylene)
PEBA	poly(ether-*b*-amide)
Nafion	poly(tetrafluoroethylene-*co*-perfluoro-3,6-dioxa-4-methyl-7-octene-sulfonic acid)
6FDA-PI	poly(2,3,5,6-tetramethyl-phenylene-2,2′-bis(3,4-carboxylphenyl)hexafluoro-propane)diimide
PI	polyimide
PEI	polyetherimide
S_{TG}	the solubility of target gas molecule in polymer
S_{TFE}	the solubility of TFE molecule in polymer
S_{TG}/S_{N2}	the relative solubility of target gas to N_2 in polymer
D_{TG}	the diffusivity of target gas molecule in polymer
D_{TFE}	the diffusivity of TFE molecule in polymer in polymer
D_{TG}/D_{N2}	the relative diffusivity of target gas to N_2 in polymer
$\alpha_{TFE/N2}$	perm-selectivity between TFE and N_2 in polymer membrane
$\alpha_{CO/N2}$	perm-selectivity between CO and N_2 in polymer membrane
$\alpha_{O2/N2}$	perm-selectivity between O_2 and N_2 in polymer membrane
$\alpha_{CO/TFE}$	perm-selectivity between CO and TFE in polymer membrane

construct a clean, compact and energy efficient TFE recovery system.

Therefore, we attempt to couple membrane unit to distillation in this paper, and the simulations accordingly have been conducted. In order to select the most appropriate membranes, an in-depth analysis of the characteristics of gas molecules involved in the separation is carried [10,11]. The permeation test with TFE distillation gas is employed to examine the performance of the selected membrane. Afterwards, a proper membrane unit is synergistically coupled to TFE distillation. The membrane unit recovers TFE from the vent gas of distillation and reintroduces the concentrated TFE into distillation. In this study, process design and optimization is achieved with the software UniSim® Design. In order to make sure that the integration process can sufficiently and efficiently recover TFE, the fluctuation in production is considered in process simulation and optimization to calculate the optimum range of membrane area.

2. Polyimide membrane for TFE recovery

Organic polymers are the principal materials used to fabricate gas separation membranes. Many polymer materials have excellent gas selectivity and can be easily processed into membranes. It is desired to find a high selective membrane for recovering TFE from the distillation vent gas.

2.1. Predicting membrane selectivity with gas critical properties

The transport parameters of the common gases (H_2, N_2, O_2, CO, CH_4, C_2H_6, C_3H_6, etc.) in polymer membrane materials have been reported in the literature. However, TFE has rarely been studied in characterizing gas separation membranes. To screen out the most practicable membrane, the common practice is doing adequate TFE permeation tests for various membranes.

According to the solution-diffusion model, polymer membrane selectivity to two gas species is characterized as the product of solution selectivity and diffusivity selectivity. These two indexes can be related to the relative condensability and the size difference of gas molecules [10–13]. Thus, the characteristics of gas molecules (T_C and V_C as listed in Table 1) can be used to roughly predict membrane selectivity. These properties are estimated by group contribution method [14,15].

Non-facilitated transport polymer membranes are usually classified as the solubility-controlled (rubbery) and the diffusion-controlled (glassy) membranes [16–20]. The prediction of membrane selectivity with gas critical properties would be progressed on the basis of this classification.

2.1.1. Solubility-controlled rubbery membranes

Three typical rubbery polymers, i.e., polydimethylsiloxane (PDMS), poly(2,2-trifluoromethyl-4,5-difluoro-1,3-dioxole-*co*-tetrafluoroethylene) (TFE/BDD87) and poly(ether-*b*-amide) (PEBA), are used to obtain the generic correlations between gas transport parameters and critical properties in the solubility-controlled membranes [21–23].

The correlation of solubility selectivity (measured by the relative solubility to N_2, S_{TG}/S_{N2}) and critical temperature (T_C) is given in Fig. 1a, and the correlation of diffusivity selectivity (scaled by the relative diffusivity to N_2, D_{TG}/D_{N2}) and critical volume (V_C) is given in Fig. 1b. It is especially emphasized that the fluorinated hydrocarbons are deviated from the generic correlation curves, as demonstrated by CF_4. The deviation of S_{TG}/S_{N2} can be ascribed to the unfavorable affinity of the hydrocarbon-based matrix to the fluorinated groups [21]. The deviation of D_{TG}/D_{N2} can be owing to the larger molecule density of fluorinated hydrocarbons.

With T_C of TFE (33.35 °C), it is observed from Fig. 1a that S_{TFE}/S_{N2} should be less than 15.0 in the rubbery polymers. After considering the poor affinity of the polymer matrix to TFE, quantified roughly with the situation of CF_4, S_{TFE}/S_{N2} is decreased to 7.0 reasonably. According to V_C of TFE (172.0 $cm^3\,mol^{-1}$), it is deduced from Fig. 1b that D_{TFE}/D_{N2} is less than 0.15. Further considering the large molecule density of TFE, by analogy with CF_4, D_{TFE}/D_{N2} is reduced to 0.12 reasonably.

Afterwards, the permeation selectivity, $\alpha_{TFE/N2}$, is approximated to about 0.84. Even though the specific properties of fluorinated hydrocarbons are ignored, $\alpha_{TFE/N2}$ cannot be larger than 2.30. In the following, the values of $\alpha_{CO/N2}$ and $\alpha_{O2/N2}$, estimated by the same way, are equal to 1.2 and 2.6, respectively. In brief, the solubility-controlled rubbery polymer membranes are poor in the ability to separate TFE from the low-boiling-point impurities. It would be inadequate to employ this type of membranes for TFE recovery.

Table 1
Molar fractions and molecular properties of components in TFE distillation vent gas.

Molecule	Content/mol%	Molar weight	V_C/$cm^3\,mol^{-1}$	T_C/°C
TFE	61.00	100.02	172.0	33.35
CO	38.71	28.01	93.1	−140.2
N_2	0.23	28.01	90.1	−147.0
O_2	0.06	32.00	73.4	−118.4